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## Diffusion in diamond. I.

### Carbon isotope mapping of natural diamond

J. A. CRAVEN<sup>1</sup>, B. HARTE<sup>1\*</sup>, D. FISHER<sup>2</sup> AND D. J. SCHULZE<sup>3</sup>

<sup>1</sup> Grant Institute of Earth Science, University of Edinburgh, King's Buildings, Edinburgh EH9 3JW, UK

<sup>2</sup> DTC Research Centre, Belmont Road, Maidenhead SL6 6JW, UK

<sup>3</sup> Department of Geology, University of Toronto, Mississauga, Ontario, Canada, L5L 1C6

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#### ABSTRACT

Recent advances in ion microprobe instrumentation and techniques have enabled the mapping of C isotope ratios across the whole of a polished plate of a natural diamond from Guaniamo, Venezuela. The resultant map of C isotope variation closely matches the cathodoluminescence image of the growth structure of the diamond and, therefore, indicates an extremely limited scale of diffusion of C atoms since the time of diamond formation. This result is compatible with the limited mobility of N atoms shown by the IaAB aggregation state of the diamond. Inclusions in the diamond are eclogitic, in common with many Guaniamo diamonds with temperatures of formation of around 1200°C. At such temperature the IaAB aggregation state indicates a mantle residence time on the order of 1 Ga. Such temperatures of formation and mantle residence times are common to many natural diamonds; thus the extremely limited diffusion of C isotopes shown by the mapping indicates that many diamonds will retain the C isotope compositions of their initial formation.

**KEYWORDS:** diffusion, diamond, ion microprobe, C isotope mapping.

#### Introduction

THE diffusion of C atoms in diamond is of particular interest to both materials scientists and Earth scientists. From the materials viewpoint, atom mobility in diamond affects its rheological and electrical properties and, therefore, its strain and electro-magnetic characteristics (e.g. Chrenko *et al.*, 1977; Stoneham, 1992). From the geochemical viewpoint, C isotope compositions of natural diamonds are widely viewed as a guide to the circumstances of diamond growth and to fluid compositions in the Earth's mantle (e.g. Deines, 1980; Galimov, 1991; Kirkley *et al.*, 1991). Therefore, it is of interest to know whether or not diffusion might modify initial isotopic signatures during long periods of mantle residence at high temperatures.

Studies of inclusions in natural diamonds show that the mantle temperatures where they originate are commonly 1100–1300°C and sometimes more, and their ages commonly range from ~1 to 3.5 Ga (e.g. Harris, 1987; Gurney, 1989; Pearson *et al.*, 1999; Richardson *et al.*, 1999; Shirey *et al.*, 2004; Gurney *et al.*, 2005), whilst the ages of eruption of diamonds from the Earth's mantle to surface are often less than 400 Ma. (Stachel and Harris, 2008). Thus, it appears that natural diamonds commonly have mantle residence ages of 500 to several 1000 million years. Under these circumstances, it is known that N atom impurities in natural diamonds undergo progressive aggregation from single atom defects on lattice sites to aggregates of two or more atoms (e.g. Evans, 1992; Mainwood, 1994). Single C atoms are expected to diffuse in similar manner to single N atoms on lattice sites. However, while the formation of N clusters leads to the further immobility of the N atoms, this effect will not occur for the dominant C

\* E-mail: b.harte@ed.ac.uk

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atoms. Hence, under mantle conditions the possibility of substantial C atom mobility arises (Harte *et al.*, 1999).

A number of experimental, theoretical and computational estimates of diffusion of atoms between diamond lattice sites have been made and span many orders of magnitude (Fig. 1). Experimental investigations are difficult, due to slow diffusion and short-term laboratory experiments require very high temperatures. To put the estimates of Fig. 1 into context, we can calculate approximately the diffusion coefficient ( $D$ ) necessary to give near homogenization across 1 mm in 1 Ga, using the approximation from Crank (1975)  $x^2 = Dt$  (where  $x$  is distance and  $t$  time). In Fig. 1, two such values of  $D$  are plotted, one for a grain of spherical shape ( $0.4x^2 = Dt$ ) and one for a slab ( $1.5x^2 = Dt$ ). These calculated values plot largely below the experimental values for atom diffusion in Fig. 1, particularly those  $>1000^\circ\text{C}$  appropriate for natural diamond crystallization in the mantle. This implies the likelihood of substantial C diffusion under mantle conditions, but evidence of such diffusion has not so far been documented for natural diamonds.

The constraints on C atomic mobility in diamond have been directly relevant to several studies pursued in the Edinburgh Materials and Micro-Analysis Centre (EMMAC) in recent years,

and as a consequence two lines of further investigation have been followed:

(1) An empirical test of C mobility by detailed mapping of C isotope variation across a natural diamond and comparison of this variation with the growth zone structure of diamond as seen in cathodoluminescence (CL).

(2) New experimental work, at high temperatures and pressures.

Both take advantage of recent developments in instrumentation and techniques. The mapping of natural isotope variations across a crystal on a small scale has only recently become possible using ion microprobe (SIMS – secondary ion-mass spectrometry) techniques. For the experimental work, advantage has been taken of recent developments in chemical vapour deposition (CVD) of diamond to prepare a clean sharp diffusion couple of contrasting C isotope composition. This paper reports the result of the empirical experiment, and another paper (Harte *et al.*, 2009) presents the high- $P$ - $T$  experimental results.

To date, ion microprobe determinations of C isotope ratio in diamonds have been done by analyses at selected points across polished diamond plates. Studies of different diamonds have shown that C isotope compositions may or may not show variations which reflect the growth

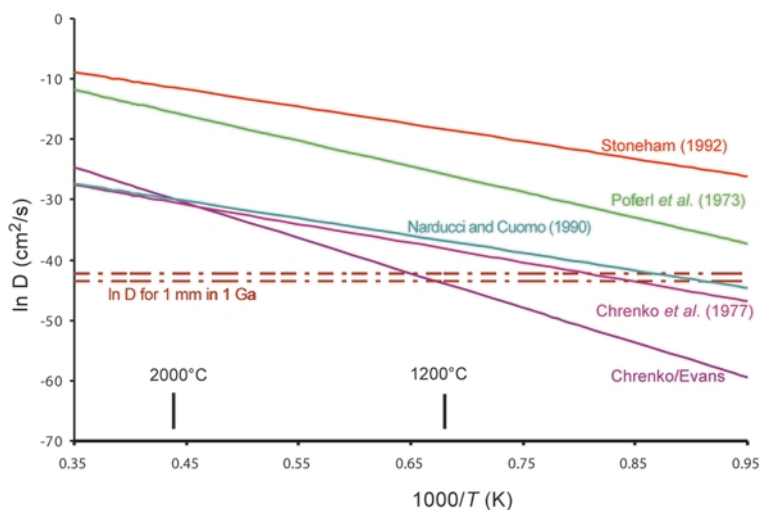


FIG. 1. Arrhenius plot of diffusion data for diamonds taken from the literature (Stoneham, 1992; Pofert *et al.*, 1973; Narducci and Cuomo, 1990; Chrenko *et al.*, 1977). The line labelled Chrenko/Evans combines the diffusion coefficients estimated by Chrenko *et al.* (1977) with the estimate of activation energy of Evans (1992). The closely spaced pair of brown dashed lines indicate the minimum  $\ln D$  value for virtually complete homogenization of C isotopes on a scale of 1.0 mm in a time of 1.0 Ga, calculated using the approximations  $1.5x^2 = Dt$  (upper line) and  $0.4x^2 = Dt$  (after Crank, 1975), where  $x$  is distance and  $t$  is time). Adapted from Harte *et al.* (1999).

zone structure seen in CL. Harte *et al.* (1999) often found near constant  $\delta^{13}\text{C}$  across complex CL growth patterns. In other cases, gradual variations exist (e.g. Hauri *et al.*, 2002; Zedgenizov *et al.*, 2006); and in some cases there appear to be sharp changes in isotope composition between cross-cutting growth zones (e.g. Fitzsimons *et al.* 1999; Schulze *et al.*, 2004). These differences may arise from a variety of causes including variations in: growth conditions, multiple growth phases, temperatures of formation and storage of the diamonds, as well as differences in the age of the diamonds. Thus, diamonds formed and stored at relatively low temperatures and kept at mantle conditions for short periods of time might preserve original isotope compositions, whilst those kept at high-temperature conditions for long periods of time within the mantle might become modified by diffusional exchange. In order to resolve this issue further, we have used the recent advances in ion microprobe instrumentation to map in detail the variation in C isotope compositions across the whole of a well characterized natural crystal, which shows a coherent and intricate pattern of growth zone structure as seen by cathodoluminescence (CL), and which is believed to have had a high-temperature history in the mantle.

## Sample description

The crystal chosen for investigation comes from the Guaniamo area of Venezuela (Sobolev *et al.* 1998; Kaminsky *et al.*, 2000), and belongs to the suite of diamonds referred to by Schulze *et al.* (2003, 2004, 2006). Like most of the diamonds from this locality, the crystal contains inclusions of eclogitic paragenesis, including clinopyroxene, coesite and kyanite (Fig. 2), and is believed to have crystallized under mantle conditions. The coesite inclusions in this diamond have previously been analysed by ion microprobe for oxygen isotopes and show extremely large  $\delta^{18}\text{O}$  values with an average of 16.1‰, strongly indicating that material forming the diamond and inclusions had a crustal origin (Schulze *et al.*, 2003). Temperatures of formation calculated for co-existing garnet and clinopyroxene crystals in the Guaniamo eclogitic diamond suite are largely constrained to the range 1150–1220°C, for pressures of 5.0–5.5 GPa (Sobolev *et al.*, 1998; Kaminsky *et al.*, 2000), and a Proterozoic age for diamond formation is suggested (Schulze *et al.*, 2006).

## Methods

### Carbon isotope measurements.

Ion microprobe measurements were made with the Cameca ims 1270 (#309) ion microprobe at the Grant Institute of Earth Science, School of GeoSciences, University of Edinburgh. The recent developments in SIMS isotope analysis embodied in the 1270 instrument allow rapid, high-precision analyses to be collected automatically, with good instrument stability, over periods of many hours. It was this combination of features that allowed us to analyse a grid of 567 point analyses on the diamond, whilst at the same time repeatedly referring to standard crystals for calibration. From the grid a detailed map of C isotope variation was constructed.

The diamond crystal (Sch 13-127-16) selected for measurement was mounted in indium between two pieces of 'synthetic A' diamond standard with  $\delta^{13}\text{C}$  of  $-23.924\text{‰}$  (Harte *et al.*, 1999). Point determinations on the sample were made principally at 100  $\mu\text{m}$  intervals along line transects which were themselves 100  $\mu\text{m}$  apart – making a grid of 25 lines with up to 24 points per line (see Fig. 2). Five measurements were made on the standard crystals at the start and end of each line, thereby enabling calibration of the sample measurements for each line against 10 standard measurements. A focused  $^{133}\text{Cs}^+$  primary beam with a current of  $\sim 5\text{ nA}$  was used. The field aperture was 4000  $\mu\text{m}$  and the imaged field 30  $\mu\text{m}$ . The secondary ions were extracted at 10 kV, and  $^{12}\text{C}^-$  ( $\sim 9.0 \times 10^8$  cps) and  $^{13}\text{C}^-$  ( $\sim 9.0 \times 10^6$  cps) were monitored simultaneously on dual Faraday cups (L/2 and H/2). Each analysis involved a pre-sputtering time of 20 s, followed by automatic secondary beam and entrance slit centring. Data were collected in two blocks of five cycles with a counting time of 4 s for each cycle. The internal precision of each analysis is  $<0.1\text{‰}$ . All data were corrected for instrumental mass fractionation (IMF) by being normalized to the 'synthetic A' standard described above.

### Nitrogen determinations

To characterize the diamond further, determinations were made of N abundance by both FTIR and ion microprobe, and of N aggregation state by FTIR. The FTIR spectra were acquired at the DTC Research Centre, Maidenhead, using a Nicolet Magna 750 spectrometer coupled to a NicPlan microscope. The frequency range of

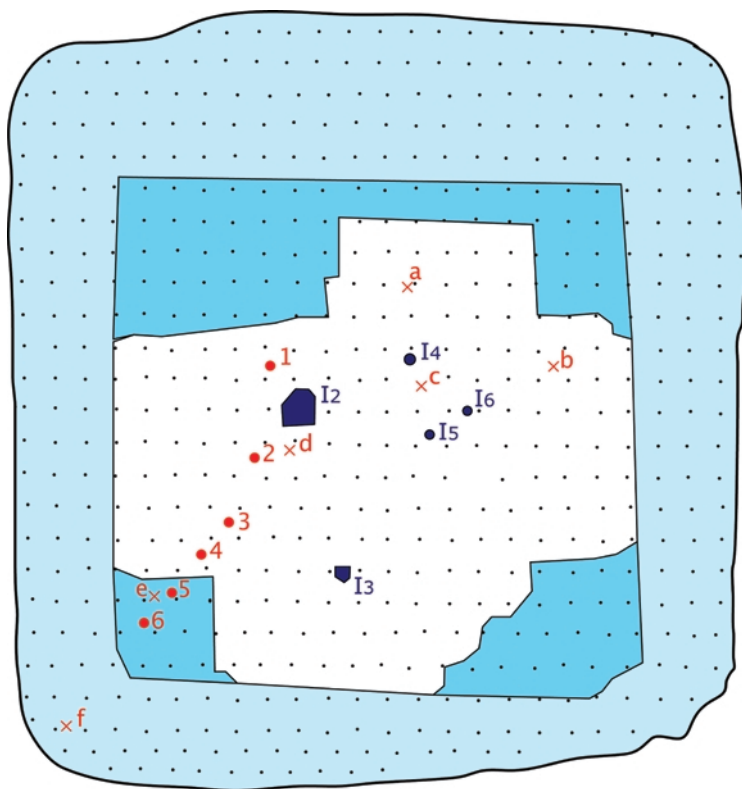


FIG. 2. Tracing of the polished surface of diamond Sch 13-127-16. The major groups of Cl zones are shown in colour (compare with CL image of Fig. 3), and the positions of mineral inclusions visible in this plate are marked in dark blue with I numbers ( $I_2$  and  $I_6$  are clinopyroxenes,  $I_3$  and  $I_4$  are coesites, and  $I_5$  is kyanite). Red numbers show the location of FTIR measurements for nitrogen aggregation state and nitrogen abundance. Red letters show the location of ion microprobe analyses of nitrogen abundance (data in Table 1). The small dots show the grid of the ion microprobe point analyses (generally 100  $\mu\text{m}$  spacing) for carbon isotope composition (see text). The diamond is 2.6 mm across at its widest.

650–4000  $\text{cm}^{-1}$  was covered at 2  $\text{cm}^{-1}$  resolution, with the receiving aperture corresponding to a 50  $\mu\text{m}$  square on the polished sample surface. The locations of analysis points are shown by red numbers in Fig. 2. Decomposition of the spectra to yield relative concentrations of N in A and B defects, and total N, was done using a spreadsheet developed by David Fisher at DTC, based primarily on the studies of Woods (1986) and Boyd *et al.* (1995).

Nitrogen concentrations were determined by ion microprobe using a Cameca ims-4f at the Grant Institute of Earth Science, School of GeoSciences, University of Edinburgh. Measurements were made of both  $^{12}\text{C}^{14}\text{N}$  molecular peak and  $^{13}\text{C}$  peak and calibrated

against standard measurements (Harte *et al.*, 1999; Fitzsimons *et al.*, 2000). The analyses were performed at relatively high mass resolution ( $m/\Delta m \sim 7500$ ) so as to distinguish  $^{12}\text{C}^{14}\text{N}^-$  from  $^{13}\text{C}_2^-$ . A  $\text{Cs}^+$  primary beam, with a diameter  $\sim 20 \mu\text{m}$ , a current of 8 nA and a net accelerating potential of +14.5 kV was used. Only the central 8  $\mu\text{m}$  of the sputtered area was analysed and counted by electron multiplier. The secondary ion acceleration potential was  $-4.5 \text{ kV}$ .

## Results

### Pattern of C isotope variations

The C isotope compositions show a relatively wide range of  $\delta^{13}\text{C}$  from  $-9.8$  to  $-18.3\text{‰}$ , and

this allows construction of a detailed map from the 567 point analyses. The CL image of the polished diamond surface is shown in Fig. 3, and the C isotope map in Fig. 4. The pattern of C isotope variation across the polished diamond surface closely follows the pattern of the CL image, including detail of the shapes of the uniform outer CL zone and the inner cross.

#### Nitrogen concentrations and aggregation states

The N data collected by FTIR and ion microprobe are given in Table 1, and cover the central area of the diamond together with a transect to the southwest corner (Fig. 2). Both types of measurement reveal wide variations in  $N_{\text{ppm}}$  within the central cross-shaped area. This accords with the marked variations recorded by CL (Fig. 3), since previous ion microprobe studies have shown a close correspondence between CL brightness and N abundance (e.g. Harte *et al.*, 1999; Hauri *et al.*, 2002). In the region of dark CL towards the bottom left corner of the diamond (Figs 2 and 3), ion microprobe measurement (point e) gives an expected very small N abundance to match the dark CL appearance. However, the adjacent FTIR points (5 and 6) give large values of 515 to 640  $N_{\text{ppm}}$ , more like the adjacent inner bright CL region. The much larger abundance found by FTIR is probably due to the fact that FTIR is a transmission technique detecting N across the thickness of the cut diamond, whilst the CL and ion microprobe are only surface analysis techni-

ques. Ion microprobe analysis indicates that the outer relatively homogenous region of the diamond has an exceptionally large N content, but no data could be obtained by FTIR on this zone because it is underlain by the steeply sloping edge of the diamond. Table 1 also gives absorption data for A (a pair of N atoms) and B (four N atoms and a vacancy) centres of N aggregation, for those sample locations where good spectral fits were obtained. They indicate a Type IaAB diamond with substantial amounts of N in both A and B aggregation states;  $N_B/(N_A+N_B)$  varies from 41–48%.

#### Discussion

The close matching of spatial arrangements seen in the CL image (Fig. 3) with those found by the C isotope mapping (Fig. 4) argues strongly for the preservation of C isotope compositions since the time of growth of the diamond. The half-spacing of C isotope measurements was 50  $\mu\text{m}$ , and the sharpness and close correspondence of the images suggest that C isotope mobility was less than this distance.

At the same time, the diamond is of Type IaAB. Given that N is considered to enter the diamond lattice initially as single substitutional atoms (Evans, 1992; Mainwood, 1994) and then undergo aggregation, it is clear that N diffusion has occurred in diamond Sch 13-127-16. This mobility is dependent on high temperatures and, therefore, is diagnostic of storage of the diamond

TABLE 1. Nitrogen data on diamond Sch 13-127-16.

Location	$N_{\text{Tot}}$ (at. ppm)	$N_A$ – at. ppm in A centre	$N_B$ – at. ppm in B centre	$N_B/(N_A + N_B)$
(1)	37.6	—	—	—
(2)	33.1	—	—	—
(3)	106.2	—	—	—
(4)	397.0	207.2	189.8	0.48
(5)	516.6	306.2	210.4	0.41
(6)	636.6	372.3	264.4	0.42
(a)	132.8	—	—	—
(b)	180.1	—	—	—
(c)	24.5	—	—	—
(d)	4.9	—	—	—
(e)	1.1	—	—	—
(f)	1195.7	—	—	—

Points (1) to (6) determined by FTIR

Points (a) to (f) determined by ion microprobe.



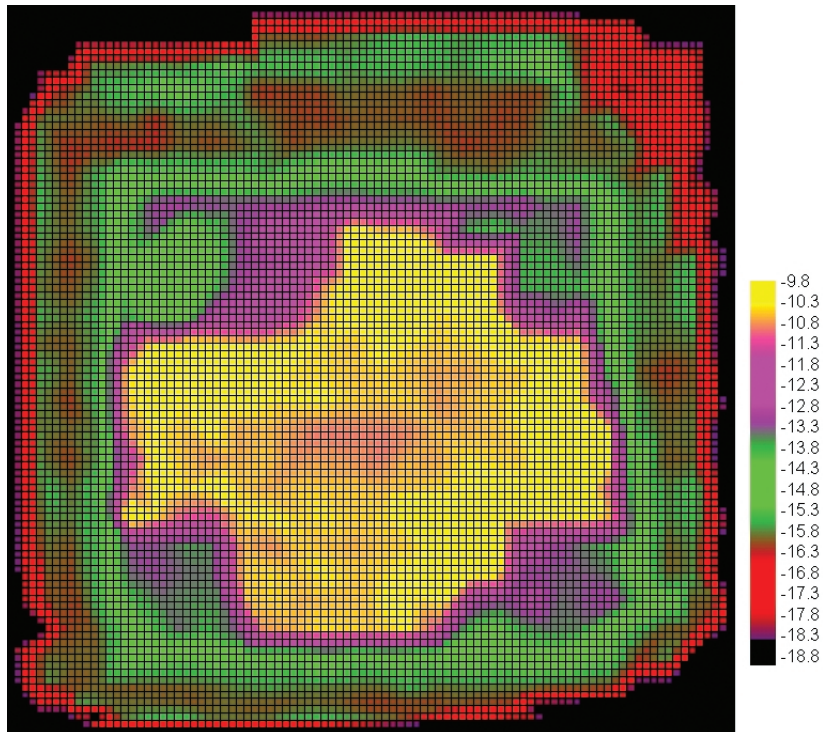
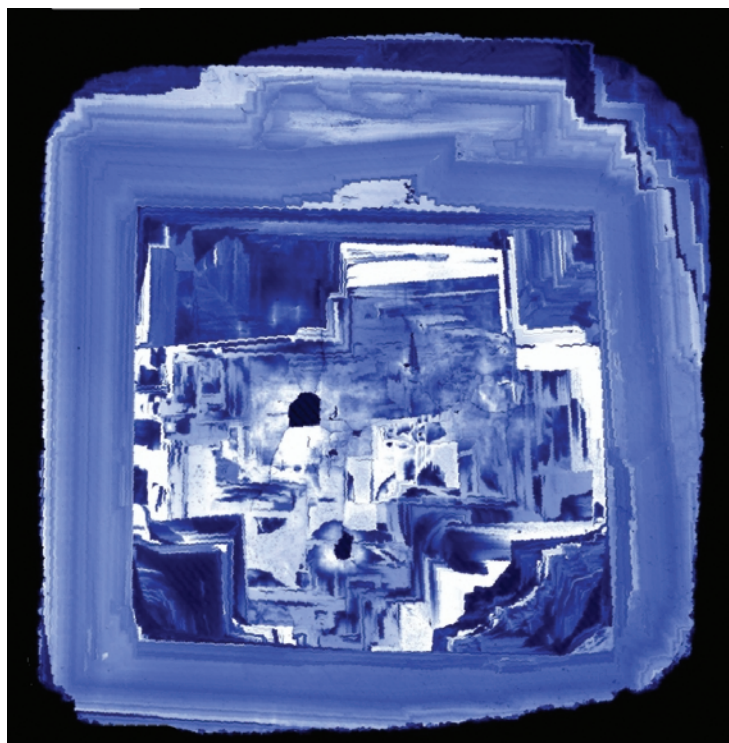


FIG. 3 (*facing page upper*). Cathodoluminescence (CL) image of polished surface across the centre of diamond Sch 13-127-16. The positions and nature of inclusions may be seen in Fig. 2. Diamond is 2.6 mm across.

FIG. 4 (*facing page lower*). Variations in  $\delta^{13}\text{C}$  across the polished surface shown in CL in Fig. 3. The overall range in  $\delta^{13}\text{C}$  ‰ is from  $-9.8$  (yellow) to  $-18.3$  (red-purple).

under mantle conditions (e.g. Taylor *et al.*, 1990; Evans, 1992). The calibrations of Taylor *et al.* (1990), for  $45\% \text{N}_\text{B}/(\text{N}_\text{A}+\text{N}_\text{B})$ , and  $\sim 300_{\text{ppm}} \text{N}$  (cf. Table 1) at the temperatures of the  $1150\text{--}1200^\circ\text{C}$  appropriate to Guianamo eclogitic diamonds, indicate mantle residence times of  $\sim 1$  Ga. These estimates are only approximate, but they clearly indicate that sample Sch 13-127-16, like many natural diamonds, has a very long mantle history at high temperatures.

In comparing the apparent C atom immobility with the N atom mobility, it is essential to remember that the scale of N mobility is self-limiting. As soon as N atoms encounter one another they will aggregate, and then, with time, proceed to greater aggregation states. So, a progression from single N atoms to dominantly A aggregates and then dominantly B aggregates is expected with time at high temperature. But with progressive aggregation, the mobility of N atoms is much reduced (Evans, 1992; Mainwood, 1994). The scale of mobility of N atoms is therefore dependent upon their spacing and the chance of them meeting in random walk diffusion. Even with average concentrations of N of only 50 ppm, N atoms will be spaced distinctly  $<1 \mu\text{m}$  apart, and thus their mobility as single atoms will be restricted to this scale (Harte *et al.*, 1999). The evidence of limited C atom mobility indicated by the diamond image is, therefore, not at variance with the evidence of N atom mobility leading to N aggregation.

## Conclusions

For the first time, we have been able to make a detailed mapping of variations in C isotope ratio across the whole of a polished plate of a natural diamond. The diamond investigated (Sch13-127-16) comes from the Guianamo province of Venezuela, and shows silicate inclusions typical of many eclogitic diamond suites worldwide, together with N abundances and an aggregation state (IaAB) common to many natural diamonds. These features indicate formation temperatures of  $\sim 1200^\circ\text{C}$  and a mantle residence time of the order of 1000 Ma.

The variation in C isotope ratio shown by the mapping closely matches the growth structure shown by the CL image of the diamond, and therefore, provides no evidence of C diffusion since the time of the diamond's formation. This is compatible with evidence of N atoms undergoing aggregation under mantle conditions, because such N atom mobility is expected to be on the sub-micron scale.

Thus, the detailed C isotope mapping provides strong evidence that many natural diamonds will essentially preserve their initial C isotope signatures, and that those signatures will be representative of the growth conditions of the diamond.

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